Development of Mechanistic-based Models of Disinfectant and Disinfectant By-product Formation

Project Scope

The water industry faces new challenges in understanding and controlling disinfection by-product (DBP) formation as additional information becomes available regarding the health concerns associated with exposures to these compounds. Accurate predictive models for DBP formation will facilitate the evaluation of treatment alternatives for disinfection and DBPs. For this reason, EPA developed a water treatment plant simulation model (*Journal of the American Water Works Association* 1992; 84[11]:78) that incorporates the then-current state of knowledge for predicting DBP formation based upon the water quality entering a treatment plant, chemical dosages applied at various locations within the treatment process, and the retention times in these processes. EPA used this model for conducting regulatory impact assessments in support of developing DBP regulations. However, EPA's DBP modeling approach is empirical (based on statistical relationships fit to the data), rather than mechanistic. The overall objective of this research project was to develop and calibrate an accurate mechanistic kinetics model to predict the formation of several chlorinated DBPs of interest. The models developed under this grant can predict DBPs, including four trihalomethanes (THM) species (THM4) and nine haloacetic acid (HAA) species (HAA9), as a function of dissolved organic carbon (DOC), disinfectant level (type and dosage), reaction time, temperature, pH, and bromide concentrations. The project had four sets of specific objectives:

1. Compile existing databases on DBP formation experiments into a single "Unified Database"; use some of the compiled data to develop and/or verify mechanistic models of DBP levels equations; identify data deficiencies.
2. Conduct controlled bench-scale experiments with raw/untreated water to track the amount (mg/L) and chemical structure of natural organic matter (NOM)/DBP precursors during different treatment processes; quantify transformations in NOMs and their properties.

Grant Title and Principal Investigator

Mechanistic-based Disinfectant and Disinfectant By-product Models for Chlorine Decay and Regulated DBP Formation Derived from Free Chlorinations (EPA Grant #R826831)

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Key Findings and Implications

- A Unified Database of chlorine decay and DBP formation kinetics from previous studies was compiled and is available to other researchers.
- WTP Model Version 2.1 software for predicting chlorine decay and DBP formation, using empirical and mechanistic models was designed and tested.
- Bench-scale experiments and previous studies support the mechanistic model that DPB formation reactions occur on two timescales, fast (minutes) and slower (hours to days).
- The mechanistic models developed by the investigators were more accurate at predicting DBPs in specific source waters, compared to power-function empirical central-tendency models (which were somewhat more accurate in predictions for waters grouped from different geographic sources).

Publications include 1 Ph.D. dissertation, 3 masters theses, and 10 conference presentations.

Project Period: September 1998 to August 2000

Relevance to ORD's *Drinking Water Research Multi-Year Plan* (2003 Edition)

This project contributes directly to the third of three Long-term Goals for drinking water research: (3) by 2009, provide data, tools, and technologies to support management decisions by the Office of Water, state, local authorities, and utilities to protect source water and the quality of water in the distribution system.

Disinfection by-products in drinking water supplies have been linked to human health concerns. This project provided experimental evidence for slow and fast DBP formation reactions, which the investigators used to build a computer model that can predict chlorine decay and DBP formation during drinking water treatment. WTP Model Version 2.1 supports both mechanistic- and empirical-based algorithms and provides the user the opportunity to specify input parameters directly or to run the model with default values. This software tool should assist EPA's Office of Water, state, local authorities, and utilities in characterizing DBP formation potential and ensuring safe drinking water.

3. Develop and calibrate numerical models for predicting the behavior of disinfectants (free-chlorine) and the formation of DBPs (THMs and HAAs); experimentally assess inorganic reactions, disinfectant decay, DBP formation, and DBP stability; and statistically compare model parameters for DBP formation against NOM properties.
4. Develop an easy-to-use computer model capable of predicting DBP formation—through a combination of mechanistic subroutines—as a function of disinfectant decay and water quality parameters.

Project Results and Implications

The project results summary is presented in four sections corresponding to the four specific objectives listed above.

Database Compilation: The investigators compiled data from published studies on DBP formation. It includes the following information: (a) water identification categories (source ID, type of treatment, and date); (b) water quality data (DOC, UVA, pH, temperature, ammonia, and bromide levels); (c) chlorination conditions (dose, reaction time, residual); and (d) byproduct formation (individual and total THM and HAAs). The Database contains data from over 2,500 chlorination laboratory experiments and over 500 sets of data from full-scale treatment plants, representing work in the United States, Canada, and New Zealand. Researchers interested in using the Unified Database should contact Paul Westerhoff at P.WESTERHOFF@asu.edu.

Formulation of Mechanistic Models

Trends observed from analysis of the Unified Database were used to formulate mechanistic models for DBP formation. The investigators used chemical rate laws for reactions between chlorine, bromine, and NOM to formulate the mechanistic model, which incorporates 70 different terms and accounts for the observation that DBP formation happens on fast and slow timescales. The reaction pathway responsible for the initial "fast" formation part of the observed DBP-versus-time curve is called the S_1 pathway and has a timescale of a few minutes to an hour. The pathway that results in the final "slow" formation part of the observed DBP-versus-time curve is called the S_2 pathway and has a timescale of a few hours to less than 100 hours. S_2 sites react with chlorine or bromine more slowly than S_1 sites. NOM contains a heterogeneous mixture of organic compounds with a wide variety of structures and characteristics and varies as a function of hydrology and biogeochemistry within watersheds. Reactions of model organic compounds were investigated, and the results were extrapolated for representative NOM species. For example, the S_1 and S_2 reaction pathways are resorcinol-type and β-diketones-type reactions, respectively. Evaluation of the Unified Database indicated a lack of kinetic data in the 0 to 2 hour time interval, which were critical for modeling S_1-type (fast) reactions.

Bench-Scale Experiments: The purpose of the bench-scale experiments was to characterize the reactions of a wide range of NOM from natural waters under conditions that simulated a range of treatment (NOM removal processes) and disinfection (chlorine dose) conditions representative of full-scale water treatment facilities.

NOM Sampling
Raw/untreated waters were collected from four locations around the United States: (1) Central Arizona Project (Scottsdale, AZ) a canal that is a diversion of the Colorado River; (2) Lake Houston water (Houston, TX); (3) Harwoods Mill Reservoir (Yorktown, VA); and (4) Lake Manatee (Bradenton, FL). After experimental treatments, samples were used for NOM "profiling" (molecular weight, hydrophobic/hydrophilic characterization, fluorescence spectrometry) and separate samples were used for kinetic chlorination studies (chlorine residual, THM species, HAA species).

NOM Treatment Profiling
In large batch or continuous flow laboratory experiments, each raw water was subjected to six simulated water treatment processes aimed at altering the structure of NOM in solution:

1. filtered raw water (0.1 µm Balston Ah-DH glass filter): used as a control;
2. alum coagulation (10 mg alum/mg total organic carbon): removed dissolved organic carbon (DOC) for waters with specific ultraviolet absorbance less than 2 m^{-1} (mg DOC/L)$^{-1}$, resulting in a NOM profile that was characterized by a lower averaged molecular weight, but similar polarity as untreated water;
3. ozonation (protocol based on achieving 1 log *Cryptosporidium* inactivation): reduced specific ultraviolet absorbance and shifted DOC to more polar material;
4. chemical softening (pH 11.0 with lime and soda ash addition): removed less than 15 percent of the DOC or specific ultraviolet absorbance, except in CAP water where slightly higher removals were observed;
5. 2,500 Dalton charged-surface ultrafiltration membrane separation: removed 45 percent of NOM from Central Arizona Project, 75 percent from Lake Houston, 87 percent from Harwoods Mill Reservoir, and 95 percent from Lake Manatee; and
6. 7-day powder activated carbon adsorption: preferentially removed hydrophobic NOM.

Kinetic Chlorination Experiments
Conditions were selected to be representative of actual chlorination conditions encountered at full-scale facilities, and differed from previous studies reported in the Unified Database most importantly in that fast reactions were measured. The test conditions included the following parameters:

- chlorine dose (baseline dose based upon obtaining 1 mg/L after 24 hours);
- pH (baseline was pH 7.5 [5.5 to 9.5]);
- bromide (baseline was ambient level spiked with 0.1 to 0.5 mg/L); and
- temperature (baseline was 15 °C [2 to 25 °C]).

Treated water samples were chlorinated, stored in separate BOD bottles, and kinetic samples were collected by sacrificing BOD bottles at approximately 5 min, 35 min, 60 min, 2 hr, 4hr, 8hr, 24hr, 48hr, and 100hr. Approximately 100 separate chlorination experiments were conducted, and each was analyzed for kinetic chlorine, THM, and HAA. Figure 1 presents results from one experiment as an example. The experimental observations supported the postulated two-phase (fast and slower) reactions proposed for the mechanistic model.

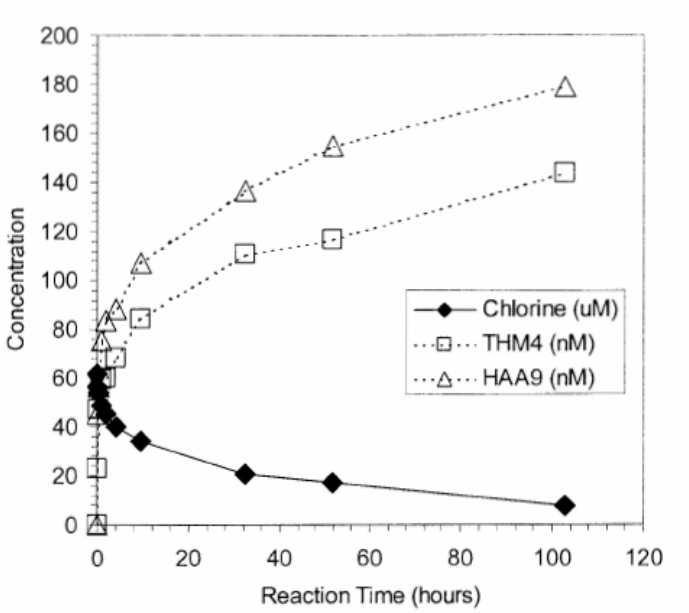

Figure 1. Representative results from kinetic chlorination bench-scale experiment (HMR water, pH=7.5, ambient bromide, chlorine dose = 2.7 mg/L, 15°C)

Trends observed for pH, temperature, and bromide were similar to those previously reported. However, this project expanded on previous studies because simultaneous measurements of chlorine and DBP under both short-term and long-term kinetic conditions were collected. The following trends were observed:

1. Lowering pH increased trichloroacetic acid (TCAA) and HAA9 formation, with a greater effect on TCAA than on HAA9. As pH decreased, so did the relative HAA rate of formation. This may indicate that intermediate structures that are present undergo base-catalyzed hydrolysis to THMs at higher pH. At low pH, hydrolysis occurs slowly, so these intermediates would instead be oxidized to form HAAs.
2. Lowering temperature generally decreased the absolute DBP formation levels, and slowed the reaction kinetics. THM and HAA kinetics were not equally affected. The results suggest that the pathway for the common precursor to THMs is more temperature sensitive than the pathway leading to HAAs.
3. Increasing bromide ion concentration lowered the concentration of chlorinated DBPs, but had relatively little effect on the total molar DBP concentration in comparison to the ambient bromide levels.

Parameterization of Empirical and Mechanistic Models: Both empirical and mechanistic models were developed from the results of kinetic batch experiments. Experimental results were parameterized based on four "cases": (I) Central Arizona Project water experiments only; (II) Lake Houston water experiments only, (III) Harwoods Mill Reservoir experiments only, and (IV) Central Arizona Project/Lake Houston/Harwoods Mill Reservoir combined water experiments. During empirical model development, linear, reciprocal, and power-function models were tested against the observed reaction kinetics. The power function relationship showed the best fits for both chlorine decay and DBP formation. Using a set of fixed values for reaction rates and reaction rate probability distributions, mechanistic models were developed to fit NOM reactive site concentrations, initial chlorine demand, and instantaneous DBP formations from experimental data, one treatment at a time. Using a consistent database (i.e., individual "case" data), both empirical and mechanistic models were compared based on paired t-test, using average error values from the model simulations of experimentally observed data. Overall, the calibrated

mechanistic model was more accurate than the calibrated empirical model, when applied to a specific water source (Cases I, II, and III), than when applied to multiple water sources (Case IV). This observation was consistent with the difference between central tendency empirical models and mechanistic models, which incorporates the variability in the character and structure of DOC, rather than simply the amount of DOC present.

Coding Mechanistic Models into EPA Water Treatment Plant Simulation Modeling Software: WTP Model Version 2.1 supports both mechanistic- and empirical-based algorithms. It provides a user the opportunity to specify input parameters directly or to run the model with default values. The default values, aside from those for S_1 and S_2, represent optimized parameter values determined through the fitting of observed data generated from the chlorination experiments described above. The outputs for WTP Model Version 2.1 are DOC, ultraviolet absorbance, chlorine residual, THM speciation, HAA speciation, and summarized level of microbial inactivation at multiple locations in a WTP process train or distribution system.

The project provides the tools to improve the understanding of DBP formation mechanisms, the effectiveness of water treatment processes, and data to inform and optimize approaches for controlling DBPs.

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For More Information

NCER Project Abstract and Reports:

http://cfpub2.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/208/report/0

Peer Reviewed Publications

None.